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Chlorinated Hydrocarbons in the Marine Environment

A Report Prepared by the

PANEL ON MONITORING PERSISTENT PESTICIDES IN THE MARINE ENVIRONMENT

of the

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Preface

It is most difficult to predict things to come for our society and for our environment. For society, the rapidity of technological advances and concomitant changes in living patterns limit our description of the future to a fraction of a decade at best. For the environment, alteration of our surroundings on a global basis takes place much more slowly, involving changes that often are imperceptible in a fraction of a decade. Our ability to manipulate the environment, climate, and various assemblages of living organisms is the hallmark of our advanced technology. The consequences are yet to be understood.

A few scientists have foretold the environmental catastrophes of the past. In the case of DDT, introduced to agriculture during World War II, there were warnings of its impending deleterious impact upon the environment several years after its first use as a pesticide. In 1946, Clarence Cottam and Elmer Higgins of the Fish and Wildlife Service wrote:

> From the beginning of its wartime use as an insecticide the potency of DDT has been the cause of both enthusiasm and grave concern. Some have come to consider it a cure-all for insect pests; others are alarmed because of its potential harm. The experienced control worker realizes that DDT, like every other effective insecticide or rodenticide, is really a two-edged sword; the more potent the poison,

the more damage it is capable of doing. Most organic and mineral poisons are specific to a degree; they do not strike the innumerable animal and plant species with equal effectiveness; if these poisons did, the advantage of control of undesirable species would be more than offset by the detriment to desirable and beneficial forms. DDT is no exception to this rule. Certainly such an effective poison will destroy beneficial insects, fishes, and wildlife.

Although many more investigations are needed in all these fields, it seems that the most pressing requirement is a study to determine the effects of DDT as applied to agricultural crops on the wildlife and game dependent upon an agricultural environment. About 80 percent of our game birds, as well as a very high percentage of our nongame and insectivorous birds, and mammals are largely dependent upon an agricultural environment. In such places application of DDT will probably be heavy and widespread; therefore it is not improbable that the greatest damage to wildlife will occur there.

Because of the sensitivity of fishes and crabs to DDT, avoid as far as possible direct application to streams, lakes and coastal bays.

Whenever DDT is used, make careful before and after observations of mammals, birds, and fishes, and other wildlife.

In the spring of 1970, the Committee on Oceanography established the Panel on Monitoring Persistent Pesticides in the Marine Environment to study the impact of DDT and other chlorinated hydrocarbons, including those of industrial origin, on the marine environment and to suggest courses of action based upon its findings. The Panel convened at Williamstown, Massachusetts, in July 1970, as participants in the Study of Critical Environmental Problems (SCEP), arranged by the Massachusetts Institute of Technology.

Through our studies and discussions, we see clearly that the observations and predictions of Cottam and Higgins have been confirmed by subsequent events. Yet man's knowledge of the fate and behavior of the chlorinated hydrocarbons in the marine environment remains inadequate. Estuarine fish-eating birds are building up such high body burdens of DDT and its degradation products that they are suffering extensive failures in the reproductive process. The mechanisms whereby DDT and its residues move from the continents to the marine environment to the fish are still not clearly understood.

This report is not intended to represent an exhaustive survey of the literature. It has been prepared to alert the community of marine scientists to one of the more serious problems arising from the dispersal of man's materials to his surroundings. Emphasis has been placed upon DDT and its degradation products because they have been the most studied to date. Through this report, the Panel has attempted to point out lacunae in man's knowledge and to suggest remedial actions. We have extended and amplified on the predictions

of Cottam and Higgins, made over 25 years ago, hoping that a similar report will not be necessary 25 years hence.

The one-month Study of Critical Environmental Problems, which covered travel expenses of the Panel members, was supported by a group of thirteen federal agencies and four private foundations. Many members of the Study contributed substantially to the Panel's report. Appendix A, on the proposed base-line sampling program, and Appendix B, on identification of globally distributed wastes in the marine environment, were prepared as working papers in cooperation with other scientists participating in SCEP and are included here with the permission of the Study. These working papers, along with others prepared for SCEP, will be published in the forthcoming MIT Press publication *Man's Impact on Terrestrial and Oceanic Ecosystems*, edited by William H. Matthews, Frederick E. Smith, and Edward D. Goldberg.

The preparation of this report was carried out as one of a series of studies under the auspices of the Ocean Affairs Board. The Board was formed in December 1970 to enlarge upon the activities and responsibilities of the former NAS Committee on Oceanography (formed in 1957). The Board operates under the joint sponsorship of the Office of Naval Research, the Atomic Energy Commission, the Department of the Interior, the National Science Foundation, the National Oceanic and Atmospheric Administration, and the Coast Guard.

PANEL ON MONITORING PERSISTENT PESTICIDES IN THE MARINE ENVIRONMENT

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Contents

CHLORINATED HYDROCARBONS IN THE MARINE ENVIRONMENT 1

Summary and Recommendations, 1
U.S. and World Production of Chlorinated Hydrocarbons, 2
Transport of DDT Residues and PCB's to the Marine Environment, 4
Distribution of Chlorinated Hydrocarbons in the Marine Environment, 6
The Ecological Impact, 8
Plankton, 8; Crustaceans, 9; Mollusks, 9; Fish, 10; Birds, 11
Biochemical Effects, 13
Recommendation: A National Effort to Curtail Long-Term Effects of Chlorinated Hydrocarbons on Community Structure, 14
Recommendation: A Chlorinated Hydrocarbon Base-line Program for the Marine Environment, 15
Recommendation: Removal of Obstacles to Public Access to Chemical Production Data, 17

APPENDIX A: PROPOSED BASE-LINE SAMPLING PROGRAM 23

Wind Systems, 23
Ocean Current Systems, 26
Organisms, 26
Rivers, 31
Glacial, Rain, and Sediment Samples, 34
Summary, 35

APPENDIX B: IDENTIFICATION OF GLOBALLY DISTRIBUTED WASTES IN THE MARINE ENVIRONMENT 37

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Chlorinated Hydrocarbons in the Marine Environment

SUMMARY AND RECOMMENDATIONS

The oceans are an ultimate accumulation site for the persistent chlorinated hydrocarbons. As much as 25 percent of the DDT compounds produced to date may have been transferred to the sea. The amount of DDT compounds in the marine biota is estimated to be less than 0.1 percent of total production, yet this amount has produced a demonstrable impact upon the marine environment.

Populations of fish-eating birds have experienced reproductive failure and decline. With continued accumulations of persistent chlorinated hydrocarbons in the marine ecosystem, additional species will be threatened. Continued release of these pollutants to the environment can only accelerate the accumulation of unacceptable levels of persistent chlorinated hydrocarbons in the tissues of marine food fish.

Certain risks in the utilization of chlorinated hydrocarbons are especially hard to quantify, but they require serious consideration. The rate at which such substances degrade to harmless products in the marine system is unknown; the half-lives of some of the more persistent materials are certainly of the order of years, and perhaps even

of decades or centuries. If most of the remaining 75 percent of the persistent chlorinated hydrocarbons is now in reservoirs that will in time transfer their contents to the sea, we may expect an increased level of these substances in marine organisms, despite future improvements of manufacturing practices. In fact, if these compounds degrade with half-lives of decades or longer, there will be no opportunity to redress the consequences.

The more the problems are studied, the more unexpected effects are identified. In view of the findings of the past decade, our prediction of the potential hazards of chlorinated hydrocarbons in the marine environment may be vastly underestimated.

The Panel makes the following recommendations, which will be developed and expanded in the remainder of the report:

- A massive national effort should be made immediately to effect a drastic reduction of the escape of persistent toxicants into the environment, with the ultimate aim of achieving virtual cessation in the shortest possible time.
- Programs should be designed both to determine the rates of entry of each pollutant into the marine environment and to make base-line determinations of the distribution of the pollutants among the components of that environment. These should be followed by a program of monitoring long-term trends in order to record progress and to document possible disaster.
- The laws relating to the registration of chemical substances and the release of production figures by government should be examined and perhaps revised in light of evidence of environmental deterioration caused by some of these substances.

U.S. AND WORLD PRODUCTION OF CHLORINATED HYDROCARBONS

The U.S. production figures for DDT, for the aldrin–toxaphene* group, and for polychlorinated biphenyls (PCB's) are presented in Table 1. The United States utilizes 70–80 percent of its production of the aldrin–toxaphene group and about 30 percent of the DDT manufactured. The remaining materials are exported (Stickel, 1968).

It is difficult to collect world production data for these materials because the information available is inadequate. Although some

*Includes aldrin, chlordane, dieldrin, endrin, heptachlor, and toxaphene.

TABLE 1 U.S. Production of Chlorinated Hydrocarbons, in Units of 10^9 g/yr

Year	DDT[a]	Aldrin–Toxaphene Group[a]	PCB[b]
1968	63.4	52.7	5
1967	47.0	54.6	–
1966	64.2	59.3	–
1965	64.0	54.0	–
1964	56.2	47.9	–
1963	81.3	48.2	–
1962	75.9	48.3	–
1961	77.9	47.2	–
1960	74.6	41.2	–
1959	71.2	39.5	–
1958	66.0	44.7	–
1957	56.6	34.3	–
1956	62.6	39.4	–
1955	59.0	35.0	–
1954	44.2	20.5	–
1953	38.4	–	–
1952	45.4	–	–
1951	48.2	–	–
1950	35.5	–	–
1949	17.2	–	–
1948	9.2	–	–
1947	22.5	–	–
1946	20.7	–	–
1945	15.1	–	–
1944	4.4	–	–
Total	1,220.0	670.0	5

[a]Chemical Economics Service, Department of Business and Industrial Economics, Stanford Research Institute (1951).
[b]Estimate based upon consumer information.

yearly figures may be found for a given country, comprehensive data for the major producers have not yet been compiled, hampering mass-balance calculations for dispersion of these materials around the earth and making an understanding of their behavior in nature difficult. An urgent need for such data is clear. Even more pressing is the need for the production figures for the polychlorinated biphenyls, which have been in use since the early 1930's.

An inspection of the production and utilization figures that were available to us (Food and Agriculture Organization, 1969) suggests

that the total world production of DDT and the aldrin–toxaphene group is probably no more than one and one half times that of the United States. Thus, as a first approximation, the integrated world production (i.e., the total amount since production began) of DDT is 2.0×10^{12} g, and the production of the aldrin–toxaphene group is 1.0×10^{12} g. The production rate used in calculations, both for DDT and for the aldrin–toxaphene group, is 10^{11} g/yr.

TRANSPORT OF DDT RESIDUES AND PCB'S TO THE MARINE ENVIRONMENT

The principal routes for transport of DDT residues* from places of application on land to the ocean are rivers, sewage outfalls, and the atmosphere.

Total annual surface runoff of water from all continents has been estimated at 3.7×10^{19} cc. The maximum concentration of DDT residues in water reported in a survey of rivers of the western United States was about 100 parts per trillion (Manigold and Schultze, 1969; Bailey and Hannum, 1967). If all rivers of the world contained this maximum, 3.7×10^{9} g of DDT residues (approximately 3 percent of the annual production of the world) would be transported annually to the sea. This figure is probably inflated, perhaps by a factor of 10. A more conservative figure may be reached by observing that DDT residues transported by the Mississippi River into the Gulf of Mexico have been estimated at 10^{7} g annually (Risebrough *et al.*, 1968b). The total river transport of DDT residues from the continental United States might be ten times that of the Mississippi, approaching 10^{8} g. Domestic U.S. use of DDT between 1961 and 1968 has ranged between 5 and 8×10^{10} g/yr, thousands of times more than can be carried in the rivers; therefore, probably only about 0.1 percent (10^{8} g) of the annual production of DDT reaches the oceans by surface runoff.

The contribution of industrial effluent to hazardous pollution of the sea or of rivers that enter the sea cannot be quantitatively incorporated into the balance sheet for the oceans, but it cannot be disregarded. In Great Britain the source of chlorinated hydrocarbon residues found in the Firth of Clyde was traced (Holden, 1970), re-

*DDT residues is a term defining DDT, DDE, and DDD. DDD and DDE are metabolites of DDT, and DDD is also a pesticide in its own right.

sulting in the discovery that approximately 1 ton of PCB per year was dumped in the ocean with the sewage sludge from Glasgow sewage treatment plants. A comparable amount was dumped into the North Sea from the wastes of Manchester and into the Thames estuary from the wastes of London. Individual factories could not be identified as the source because many use the same sewers. In the United States, PCB's in aquatic organisms were similarly traced, disclosing a factory leakage on the Escambia River in Florida (Duke *et al.*, 1970).

DDT residues enter the atmosphere by several routes, including aerial drift during application by rapid vaporization from water surfaces (Acree *et al.*, 1963) and by vaporization from plants and soils (Nash and Beall, 1970). Once in the atmosphere, DDT residues may travel great distances, entering the sea in precipitation or in dry fallout. There are few data for estimating these rates of transfer. Sampling of DDT residues in precipitation has been most extensive in Great Britain, where total accumulation was measured at seven stations between August 1966 and July 1967. The mean concentration in those rainwater samples was 80 parts per trillion (Tarrant and Tatton, 1968), about twice that reported for meltwaters of recent Antarctic snow (Peterle, 1969). The DDT residues in south Florida precipitation averaged 1,000 parts per trillion in 18 samples taken at four sites between June 1968 and May 1969 (Yates *et al.*, 1970).

Total annual precipitation of water over the oceans has been estimated at 3.0×10^{20} cc (Sverdrup *et al.*, 1942). If this precipitation had an average concentration of DDT residues of 80 parts per trillion, a total of 2.4×10^{10} g of DDT residues would be transported annually to the oceans, about one quarter of the estimated total annual production of DDT. It is at least plausible that the atmosphere is the major route for transfer of DDT residues into the oceans.

Other chlorinated hydrocarbons with similar physical and chemical characteristics can be expected to have similar dispersal mechanisms. Dieldrin, which readily volatilizes into the atmosphere (Lichtenstein *et al.*, 1968), has been found in airborne particulates over the ocean (Risebrough *et al.*, 1968b) and in rainwater (Tarrant and Tatton, 1968). Polychlorinated biphenyls have also been detected in rainwater (Tarrant and Tatton, 1968). PCB has not yet been measured in river waters, but there is evidence that it occurs in the biota of the Atlantic in quantities of the same magnitude as residues of the DDT group. The relative importance of river transport, aerial fallout, sewage outfalls, and dust discharge of PCB into the sea remains to be determined.

DISTRIBUTION OF CHLORINATED HYDROCARBONS IN THE MARINE ENVIRONMENT

Few data are available to document the concentration of chlorinated hydrocarbons (including PCB's) in the open ocean environment. However, a few observations indicate that DDT and its residues are probably distributed throughout the marine biosphere. Gray whales contain up to 0.4 ppm DDT residues in their blubber, and sperm whales, up to 6 ppm (Wolman and Wilson, 1970). Gray whales feed largely on benthic organisms in the Chukchi and Bering seas, and sperm whales feed on larger pelagic organisms. Sea birds (petrels and shearwaters), which feed on planktonic organisms far from land, have concentrations of DDT residues as high as 10 ppm (Risebrough, unpublished data). Migratory fish (tuna) carry up to 2 ppm of these same compounds in their gonads, and other marine mammals carry up to 800 ppm in their fat (Butler, 1969). In the latter two cases, it is not known whether these concentrations resulted from localized contact in coastal waters or were accumulated during the life of the organisms in the open ocean. In the coastal environment, DDT and its residues range from undetectable levels to 5.4 ppm in oysters (Butler, 1969). Concentrations within these limits are highly variable locally and vary considerably even within the same estuary.

In spite of the paucity of useful data, some assumptions can be made for the marine environment, excluding estuaries, by assigning likely values for DDT residues to the biota of the open ocean and extending the calculations to a global basis. Such computations are valuable in that they identify potential sinks and provide order-of-magnitude estimates of most probable distributions.

The following assumptions are made:

1. The standing crop of plankton (plant and animal) is 3×10^{15} g (Menzel, unpublished data).
2. The standing crop of fish is 6×10^{14} g, equal to 10 times the present annual fish harvest (Rhyther, 1969).
3. The concentration of DDT residues in plankton averages 0.01 ppm.
4. The concentration of DDT residues in fish averages 1.0 ppm.
5. A homogeneous distribution of DDT in the mixed layer (the upper 100 m of seawater, which are homogenized by the action of winds) has resulted from atmospheric transport from the continents.

By assigning the values in assumptions (3) and (4) to the calculated standing crop of organisms, (1) and (2), it is estimated that the total plankton now contain 3.0×10^7 g and fish 6×10^8 g of DDT residues, both insignificant fractions of the total annual input of these residues to the environment (10^{11} g). We propose these estimates as upper limits to the size of the pool.

With a saturation level of DDT* in water of 1 ppb (Bowman *et al.*, 1960) and the volume of the mixed layer (upper 100 m of the ocean) as 0.025×10^{24} ml, the surface waters of the ocean are capable of accommodating a load of 7.5×10^{13} g of DDT, or approximately 38 times the total production to date. There is no indication, however, that DDT introduced into the marine environment is uniformly distributed in the mixed layer. Enrichment is likely to occur in the sea's surface film, which contains fatty acids and alcohols. If this is the case, predictions indicate (a) that DDT may be stripped from this film by bacteria and phytoplankton, thus entering the food chain; (b) that it adsorbs to airborne particles that sink through the water column (in this case the compound is probably ingested by grazing organisms that do not discriminate between living and inert particles); or (c) that it codistills with water or is injected back into the atmosphere as aerosols and is redistributed, leading to neither a net increase or decrease in concentration at the surface.

Lacking any data for concentrations in the waters of the open sea, it is impossible to estimate directly how much is present that is not incorporated into living organisms. However, estimates of fallout in rain suggest that one quarter of the world's production of DDT may have entered the ocean. Its aerial distribution is probably uneven, dependent upon weather patterns and proximity to major sources of input.

If only 0.01 percent (10^8 g) can be accounted for in pelagic marine organisms, 0.50×10^{12} g (one quarter of total production) should be present in solution and in the bottom sediments. In order to balance input with accountable fractions, the surface mixed layer volume (0.025×10^{24} ml) should contain concentrations of approximately 5×10^{-12} g/ml, given a residence time of 5 years and an annual input of 0.25×10^{11} g of DDT per year.

*Saturation levels of DDD and DDE have not yet been measured.

THE ECOLOGICAL IMPACT

The acute and chronic toxicity of chlorinated hydrocarbons has been identified by observing the effects of chlorinated hydrocarbons under controlled laboratory conditions. The exposure of test populations of marine fauna to serial dilutions of these pollutants in flowing seawater has shown that they affect growth, reproduction, and mortality at concentrations currently existing in the coastal environments. These laboratory effects and their field counterparts are summarized in the following sections.

Plankton

The addition of chlorinated hydrocarbons to laboratory cultures of molluscan larvae and the phytoplankton on which they feed causes, with increasing concentrations, decreased growth rates, developmental failures, and increased mortality (Ukeles, 1962; Davis, 1961). By extrapolation, toxaphene levels observed, in one estuary of the southeastern United States in 1967, for example, were high enough to have caused the death of a majority of the phytoplankton suitable as food for molluscan larvae (Butler, 1969).

In the open ocean, phytoplankton are at the base of the food chain and may act as primary concentrators of chlorinated hydrocarbons from the water. Laboratory evidence is available demonstrating inhibition of photosynthesis in single-celled marine plants by DDT, dieldrin, and endrin (Wurster, 1968; Menzel *et al.*, 1970). It is doubtful, however, that these results are ecologically meaningful. The concentrations necessary to induce significant inhibition far exceed expected concentrations in the open ocean and exceed by ten times the solubility of DDT (1 ppb) in water. One species tested was insensitive to concentrations of all three pesticides up to 1 ppm. Therefore, toxicity may vary interspecifically, and, if not universally toxic, a chlorinated hydrocarbon might exert some control on species succession in the nearshore environment.

If chlorinated hydrocarbons are concentrated in surface oil films, it is not improbable that concentrations there may reach levels sufficient to cause acute toxicity to plants. Considering that this layer may extend 1 mm in depth, its effect would be to reduce total production within the euphotic zone (100-m depth) by about 10^{-5}. It must be borne in mind, however, that plants and bacteria may provide an effective means of extracting these hydrocarbons from the surface film. Partition coefficients have not been experimentally determined

from marine species but have been established as approximately 1,000 in the case of dieldrin for a freshwater alga (Reinert, 1967). These organisms are available as food to grazing and surface-skimming feeders. The important fact here is not the effect of chlorinated hydrocarbons on primary production, but rather that plants may be the vehicle for transferring these compounds from the water to higher trophic levels.

Experimental evidence from the calanoid copepod *Pseudodiaptomus cornatus* has shown that the development of adults from nauplii is completely blocked when hatched from egg-bearing females maintained in seawater containing 10 parts per trillion DDT (Menzel, Anderson, and Randtke, unpublished data). Significant mortality was observed at 5 parts per trillion. These concentrations of DDT are lower than expected in rainwater falling on the sea surface (80 parts per trillion). These observations cannot be applied to the open oceans, because, as noted earlier, no measurements of DDT concentrations are available from these waters.

Crustaceans

Bioassay tests show that laboratory populations of commercial species of shrimp and crabs as well as zooplankton are killed by exposure to chlorinated hydrocarbons, such as DDT and PCB, in the parts per billion range (Butler, 1964; Duke *et al.*, 1970). Continuous exposure of shrimp to DDT concentrations of 0.2 ppb caused 100 percent mortality in 18 days, and a concentration of 0.12 ppb caused 100 percent mortality within 28 days (Nimmo *et al.*, 1970). Concentrations of this magnitude have been detected in Texas river waters flowing into commercially important shrimp nursery areas (Manigold and Schulze, 1969). Certainly in such contaminated areas there are significant increases in mortalities of juvenile crustaceans. In California the declining production of Dungeness crabs may be associated with observed DDT residues in the developing larvae. Polychlorinated biphenyls (Aroclor 1254) at a concentration of 5.0 ppb caused 72 percent mortality in 20 days to test populations of pink shrimp (*Penaeus duorarum*); these shrimp had accumulated 33 ppm of the PCB in their tissues (Duke *et al.*, 1970).

Mollusks

The chlorinated pesticides and PCB's characteristically interfere with the growth of oysters. One ppb of the PCB Aroclor 1254, for

example, causes a 20 percent decrease in shell growth (Duke *et al.*, 1970). Many pesticides interfere with oyster growth at levels as low as 0.1 ppb (Butler, 1966b), in the ambient water. Mollusks generally concentrate these chemicals and thus serve as indicators of pollution levels in marine waters. Coastal monitoring samples have demonstrated that the magnitude of chlorinated hydrocarbon residues in mollusks are directly correlated with the application rates of these agricultural chemicals in adjacent river basins (Butler, 1967).

Fish

Marine fish are almost universally contaminated with chlorinated hydrocarbon residues. There is an expected concentration of such residues in lipid tissues such as the ovary. In the speckled sea trout on the south Texas coast, DDT residues in the ripe eggs are about 8 ppm. This level may be compared with the residue of 5 ppm in freshwater trout that causes 100 percent failure in the development of sac fry or young fish. The evidence is presumptive for similar reproductive failure in the sea trout. Sea-trout inventories in the Laguna Madre in Texas have shown a progressive decline from 30 fish per acre in 1964 to 0.2 fish per acre in 1969 (Table 2). It is significant that few juvenile fish have been observed there in recent years, although in less contaminated estuaries 100 miles away there is a normal distribution of sea-trout year classes (Butler, 1969).

Declines in the productivity of fish in California coastal waters have not yet been correlated with residues of chlorinated hydro-

TABLE 2 Capture of Sea Trout in Laguna Madre[a]

Year	Number of Sea Trout Captured per Acre
1964	30
1965	25
1966	12
1967	[b]
1968	2.7
1969	0.2

[a] From Butler *et al.* (1971).
[b] No data exist for 1967, as hurricanes destroyed all the fishing gear. The decline in the fishery has been only in the juvenile trout, which eliminates the possibility of over-fishing. The DDT residues in the gonads of the adult trout reach a maximum of 8 ppm prior to spawning.

carbons. However, the sale of some California mackerel has been prohibited because DDT residues exceed permissible human tolerance levels, even in the processed product.

A kill of Mississippi River fish in 1963–1964 was traced to chemicals entering the river system from an insecticide-manufacturing plant (Mount and Putnicki, 1966). Exceedingly high endrin concentrations were found in nearby sewers and in a riverside dump.

Laboratory experiments have also established the concentration of several chlorinated hydrocarbons, including DDE, that damage reproductive success of birds, fish, and marine invertebrates. Only preliminary work on the effects of PCB on marine organisms has been reported. Concentrations of one or more chlorinated hydrocarbons in species from the marine environment exceed those found to have deleterious effects in the laboratory and have been correlated with population decreases or reproductive failures of a number of marine species. Signs of incipient damage that can be expected to develop further with continuing accumulation have also been reported.

Birds

Chlorinated hydrocarbon residues have seriously affected both adult birds and their reproduction. Deaths of bald eagles (Mulhern *et al.*, 1970), common loon (Butler, 1966a), and peregrine falcons (Jefferies and Prestt, 1966) have been correlated with lethal amounts of chlorinated hydrocarbons in body tissues. Widespread mortality of many coastal birds in the Netherlands and population decline of the sandwich tern were traced to dieldrin contamination of the Dutch Wadden Sea and the coastal North Sea resulting from factory effluent. Sea eagle reproduction has failed, and outright mortality has occurred in the Baltic Sea in association with very high levels of DDT compounds and PCB in the tissues (Jensen *et al.*, 1969).

Studies of museum series of eggs indicate that eggshell thinning has occurred since the mid-1940's in a wide range of species of fish-eating birds and birds of prey. Where shell thinning has occurred, the populations have usually declined (Ratcliffe, 1967; Hickey and Anderson, 1968). Eggshell thinning and consequent population decline have been linked to chlorinated hydrocarbon residues found in eggs and in the body tissues of birds.

In experimental studies, DDE in the diet of mallard ducks resulted in thin eggshells and reduced hatching success; p,p′-DDT produced

the same effects, but to a lesser degree (Heath *et al.*, 1969). Both DDE alone and a combination of p,p'-DDT and dieldrin in the diet of American kestrels resulted in thin eggshells; the test of DDT plus dieldrin was carried out long enough to show reduced hatching success (Porter and Wiemeyer, 1969; Wiemeyer and Porter, 1970).

Black duck egg samples at Atlantic coastal sites in the United States showed highest residues of chlorinated hydrocarbons in states where duck reproduction is poorest. Nationwide sampling of wing tissues showed highest residues in the same areas (Reichel and Addy, 1968; Heath, 1969). In three states from which bald eagle eggs were analyzed, residues of DDT and dieldrin were highest in the eggs from the state where reproduction is poorest and has declined to nearly zero (Krantz *et al.*, 1970).

Samples of brown pelican eggs from 12 Atlantic and Gulf colonies showed greatest shell thinning in the Carolina colonies, where populations have declined precipitiously. On the basis of museum series, it has been determined that shell thinning has occurred in all areas (Blus, 1970; Anderson and Hickey, 1970).

In the marine ecosystems of southern California, where concentrations of the DDT compounds in fish may exceed 10 parts per million (Risebrough *et al.*, 1971), a disastrous reproductive failure occurred in 1969 among brown pelicans on Anacapa Island as a result of eggshell collapse (Jehl, 1969; Keith *et al.*, 1970; Risebrough *et al.*, 1970). In this area, the brown pelicans and double-crested cormorants are no longer able to reproduce. At most, four brown pelicans hatched in southern California in 1969 among approximately 1,200 nesting attempts (Risebrough, Sibley, and Kirven, unpublished data). In 1970, only one brown pelican hatched in 500 attempts (Gress, unpublished data). No double-crested cormorants were fledged in southern California in 1969, and only one brood was fledged in 1970 (Gress, Risebrough, Jehl, and Kiff, unpublished data). The cause in all cases was a failure of the eggs to hatch because of breakage during incubation.

Concentrations of the DDT compound DDE in the lipid fractions of the eggs were correlated inversely with shell thickness in brown pelican eggs from Anacapa Island, the Islas de Coronados in Mexico, other localities in Baja California, and four colonies in Florida (Risebrough, Gress, Anderson, and Schreiber, unpublished data). By comparing pelican eggs from California and Florida, where the relative amounts of DDE and PCB are very different, the same investi-

gators concluded that DDE is the major cause of shell thinning in the brown pelican eggs. Pelican eggs collected on Anacapa in 1962 showed a critical level of shell thinning, but less than the thinning observed in 1969 and 1970 (Anderson and Hickey, 1970). Young pelicans were still produced on Anacapa in 1963 and 1964 (Banks, 1966). From the observed relationships between DDE concentration and shell thinning it can be concluded that between 1962 and 1969, accumulations of chlorinated hydrocarbons in the southern California marine ecosystem passed a level critical to the brown pelican.

Shell thinning has also been detected in marine and coastal birds in northern California, including the common murre (Gress, unpublished data), the ashy petrel (Risebrough and Coulter, unpublished data), and the American egret (Pratt and Risebrough, unpublished data). Continued buildup of chlorinated hydrocarbons in this ecosystem and in other marine ecosystems around the world will cause reproductive failures in these and other marine species.

BIOCHEMICAL EFFECTS

Several physiological effects of chlorinated hydrocarbons could account for shell thinning and for the abnormal behavior observed in contaminated populations. In affecting nerves, chlorinated hydrocarbons, including DDE, are believed to block the ion-transport process by inhibiting one or more ATPases in the nerve membrane (Matsumura and Patil, 1969; Koch, 1969) that causes the required energy to be made available.

Transport of ionic calcium across membranes such as those in the shell gland of birds is also an energy-requiring process dependent upon membrane ATPase (Corradino *et al.*, 1968). Inhibition of these enzymes by DDE could account for the concentration-effect curves obtained for shell thickness and DDE concentration in eggs of the brown pelican, double-crested cormorant (Anderson *et al.*, 1969), and herring gull (Hickey and Anderson, 1968). DDE has also been found to inhibit the enzyme carbonic anhydrase (Peakall, 1970; Risebrough *et al.*, 1970; Bitman *et al.*, 1970), essential for the deposition of calcium carbonate in the eggshell and for the maintenance of pH gradients across membranes such as those in the shell gland. Inhibition of this enzyme by such drugs as sulfanilamide results in the production of thin-shelled eggs.

The chlorinated hydrocarbons, including DDE and PCB, induce

mixed-function oxidase enzymes in the livers of birds and mammals that hydroxylate and render water-soluble any foreign, lipid-soluble compounds (Conney, 1967; Risebrough *et al.*, 1968a; Street *et al.*, 1969). Induction is usually a temporary phenomenon, ending when the inducing materials are themselves metabolized. DDE and the more heavily chlorinated PCB molecules are comparatively resistant to degradation by the induced molecules, so they may persist as inducers for some time. The induced enzymes may therefore become constitutive.

The steroid hormones, such as estrogen and testosterone (Conney, 1967; Peakall, 1970) and thyroxine (Schwartz *et al.*, 1969), are metabolized at higher rates when these enzymes are induced. Lower estrogen concentrations are present in pigeons fed p,p′-DDT (Peakall, 1970). Birds may also show symptoms of hyperthyroidism when fed a chlorinated hydrocarbon (Jefferies, 1969; Jefferies and French, 1969).

RECOMMENDATION: A NATIONAL EFFORT TO CURTAIL LONG-TERM EFFECTS OF CHLORINATED HYDROCARBONS ON COMMUNITY STRUCTURE

These well-documented changes in the earth's living systems are part of a larger pattern of changes in the structure of the natural communities of estuaries, coastal regions, and the oceans. The pattern is familiar: it is the pattern associated with accelerated eutrophication and pollution of water bodies; it is analogous to the changes in structure of forests caused by a variety of disturbances, including ionizing radiation (Woodwell, 1970). The reduction of structure leads progressively to shorter food chains in which hardy, broad-niched species with rapid reproductive rates predominate. On land, these are the simplified, eruptive insect and rodent communities of highly disturbed areas; in water, they are the equally simplified communities of eutrophic lakes and estuaries, in which harvestable fish populations are often depressed and bird populations are dominated by scavengers such as the herring gull. The problem in water, however, is greater, since the reduction of consumer populations is accompanied by a shift in plant species to hardy algae that are not consumed by grazers; their production instead accumulates, decaying anaerobically and further reducing the potential of the site for support of man.

While such changes are caused by many factors, the accumulations of persistent chlorinated hydrocarbons in estuaries and in coastal waters have become a significant factor accelerating this pattern of change.

The panel recommends a massive national effort to effect a drastic reduction of the escape of persistent toxicants into the environment, with the ultimate aim of achieving virtual cessation in the shortest possible time. Only in this way can we hope to curtail the deleterious effects of chlorinated hydrocarbons upon community structure.

RECOMMENDATION: A CHLORINATED HYDROCARBON BASE-LINE PROGRAM FOR THE MARINE ENVIRONMENT

The paucity of analyses of chlorinated hydrocarbons in materials from the marine environment and from those parts of the atmosphere and the continental hydrosphere that provide these chlorinated hydrocarbons to the marine environment limits our ability to make judgments about their present and future impacts upon ecosystems. Any predictions about the rates of buildup in a given reservoir are somewhat speculative.

Yet, we cannot initiate an effective monitoring program until the present dissemination of these materials at the earth's surface is detailed. An entry to a reasonable monitoring program can be found in a base-line study in which the concentrations of the chlorinated hydrocarbons in geological and biological components of the marine environment, as well as in their transporting agencies, are determined. Such an investigation can conceivably be carried out in a year.

A carefully planned investigation is necessary in order to obtain a critical amount of data with the minimum expenditure of funds. By utilizing a single laboratory to manage the program, difficulties in standardization and in sample preparation and handling can be minimized. In the detailed planning and sample collection, the inputs from a variety of disciplines are necessary not only at the beginning of the work but also on a continuing basis. A large-scale program dealing with such a broad area will digress from the initial schedule of analyses as unexpected results come in.

The following outline indicates the types of samples to be obtained. We envisage perhaps a thousand analyses during the first year's base-line program. Temporal, geographic, and spatial sampling procedures will be formulated for each of the groups of substances.

Samples of transport paths
  Major wind systems (sample in dust and as vapors)
    Prevailing westerlies–the jets
    Trades
    Regional winds such as monsoons and harmattans
  Rain, snow, and dry fallout; glacial samples provide data on fallout in past (Windom, 1969)
  The major rivers of the world (dissolved, suspended and bed-load materials)
  Sewer outfalls draining directly into marine environment from major population centers of the world
  Material released either by intent (dumping of wastes) or inadvertently (PCB's from antifouling paints on ships) from vessels

Samples from reservoirs in the marine environment
  Seawater (particulate and dissolved loads)
  Isolates from air–water interface, surface-active agents, slicks
  Sediments
  The major fisheries food chains, including plankton, the harvestable material, and predators of the harvestable material
  Selected estuarine organisms, such as oysters

The frequency of samples, as a function of location, time, or type, will depend on the resources available. Reasonable emphasis should be placed on historical records of inputs to the environment through the use of glacial (permanent snowfield) samples that record the atmospheric transport of material removed by precipitation and dry fallout. Museum specimens may provide a most useful index of the past body burdens of organisms.

A base-line program for chlorinated hydrocarbons will provide samples for investigating other materials being disseminated about the world ocean that pose threats to marine organisms.

The identification of a material that may endanger an ecosystem often occurs only after substantial disseminations have been made to the environment. A bank of samples, collected in sufficient quantities, will provide a historical record of invaluable use in such instances.

Examples of other materials that might be sought are such metals as mercury, cadmium, lead, and arsenic; such industrial chemicals as methyl chloride and vinyl chloride; such widely used chemicals as dry cleaning fluids (perchlorethylene and trichlorethylene) and freon; and such dust components as asbestos and fly ash.

More detail on this proposed program will be found in Appendix A.

RECOMMENDATION: REMOVAL OF OBSTACLES TO PUBLIC ACCESS TO CHEMICAL PRODUCTION DATA

Among the causes contributing to the lack of available data on the chlorinated hydrocarbons is a legal structure that allows manufactures of a given material, when there are no more than two producers, the right to hold their production figures as privileged information.*

The Panel recognizes the economic rationale that deters the release of production figures by such manufacturers and understands that our government is charged by law with the protection of that proprietary interest. Indeed we approve the principle that governmental action should not artificially affect competition.

However, we also feel that there are times when it is not in the public interest for government to maintain as privileged data that are necessary for research into the state of our environment and for an assessment of its condition. In that regard, we recognize the possibility that it is not always competitive concerns alone that determine the less than candid posture assumed by industry concerning production figures.

We recommend that the laws relating to the registration of chemical substances and to the release of production figures by the Department of Commerce and the Bureau of the Census be re-examined and revised in the light of existing evidence of environmental deterioration. The protection afforded manufacturers by government is an artificial obstacle to effective environmental management, particularly with reference to the polychlorinated hydrocarbons. In view of other impediments—technological, methodological, and financial—such protection is clearly inappropriate.

*For example, the Monsanto Chemical Company has refused to release its production figures for PCB's, although requested to do so by many scientists and government officials.

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Appendix A Proposed Base-line Sampling Program

There are few data on the present concentrations of potentially toxic pollutants in the marine environment. Such base-line data are essential in identifying areas of needed research. However, while perhaps desirable in the future, a global monitoring program requiring great expenditures and technological advances is an inexpeditious approach to acquiring data that are needed immediately. A simplified base-line sampling program meets that need without unreasonable financial and technological strains. Moreover, such a program can provide a basis for a more ambitious monitoring system.

Guided by such concerns, we propose a one-year program to gather approximately one thousand samples from wind systems, ocean current systems, organisms, rivers, and glaciers, rain, and sediments. This proposed program would begin implementation of our recommendation for a chlorinated hydrocarbon base-line program for the marine environment.

WIND SYSTEMS

To design a network of sampling stations for measuring concentrations of gaseous and particulate pollutants in the atmosphere, the

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prevailing global wind systems must be considered in relation to the major sources of pollutants. It is also necessary to identify mechanisms by which pollutants are transported laterally and vertically and to estimate the vertical boundaries of the atmospheric layer within which appreciable vertical mixing takes place.

Most sources of airborne wastes are located on those parts of North America, Europe, and Asia (including Japan) over which there is a predominantly westerly flow. Furthermore, effluents are usually released near the ground at low speeds and, unlike emissions from volcanos, are unable to penetrate high into the atmosphere. We are primarily concerned here with the atmospheric part of the biosphere, a very thin layer bounded by the earth's surface.

The prevailing wind systems are

The tradewinds, 30°N–30°S: These easterly winds near the earth's surface decrease in strength with increasing height and become westerly except near the equator, where they retain the same direction at all heights

The westerlies, 30°N–70°N, 30°S–65°S: The westerly winds increase in strength to a height of at least 10 km

The polar easterlies, 70°N–90°N, 65°S–90°S: These shallow winds decrease in strength with height and reverse their direction at about 3 km

These major wind systems are modified by seasonal changes associated primarily with the warming and cooling of the continents (these changes result in such phenomena as monsoons) and by north–south-oriented mountain ranges that cause large-scale meandering of the otherwise zonal flow.

The lateral and vertical transport mechanisms within these wind systems are small-scale turbulence, local circulations such as ordinary convection and severe storms, extratropical cyclones within the westerlies, and easterly waves, tropical storms, and hurricanes within the tropical easterlies.

The layer within which appreciable mixing takes place may be estimated by observing the concentration of sea-salt particles at altitudes from sea level upward. Toba (1965) reports that the number of these particles of 1–10-μ radius decreases quite rapidly with altitude; for the smallest of these particles (1-μ radius), the decrease is

approximately tenfold from the sea surface up to an altitude of 6 km. For submicron-size particles, the rate of decrease with altitude is probably somewhat lower. Because of the scarcity of particles at 6 km, this appears to be an appropriate ceiling for the mixing layer.

For our immediate purpose, it is probably not necessary to measure particulates within the westerlies above an altitude of 5 km. The corresponding altitude is somewhat lower in the trade winds and the polar easterlies.

Major sources of pollutants are the United States, western Europe, the Soviet Union, China, and Japan, all located within the westerlies. Minor sources are Africa (located within the trade winds and, to a lesser extent, within the westerlies), South America (located within the trade winds and the westerlies), and Australia (located within the trade winds). Based on this distribution, we suggest the following sample network.

Location	Number of Samples				Frequency per year	Total
	Surface	500 m	1,500 m	5 km		
North America	15	7	4	2	2	56
Europe and Asia	20	10	5	3	2	76
Africa	3	0	3	3	1	9
South America	3	0	3	3	1	9
North Atlantic	5	0	3	3	1	11
South Atlantic	3	0	3	3	1	9
North Pacific	7	0	4	4	1	15
South Pacific	3	0	0	3	1	6
Australia	1	0	1	1	1	3
Arctic	1	0	0	1	1	2
Antarctic	1	0	0	1	1	2
Subtropical high-pressure cells	2	0	0	2	1	4
Total						202

Additional measurements should be obtained near the sea surface by means of research and commercial ships and at greater altitudes by means of special-purpose and commercial aircraft. Aircraft observations are, perhaps, the only observations needed above 5 km.

OCEAN CURRENT SYSTEMS

Since the pollutants of potential importance in the ocean may take a variety of forms (such as gases, solutes, particles, oils) and may enter by various paths (e.g., atmosphere, rivers, ships), a set of base-line water samples should be spaced both horizontally and vertically in such a way as to detect any of these forms. Both the physical circulation of the ocean and the distributions effected by biological transport must be taken into account so that a proper framework for assessment of the ultimate distributions in the oceans can be established.

Sampling methods, means of treatment for preservation, and transpcrt for analysis are not discussed at this time. When such problems are confronted and the suggestions for sampling of other parts of the environment compared, some modifications in sampling methods can be expected.

In establishing a tentative framework for base-line sampling of ocean water, three kinds of vertical spacing are suggested. The first is simply a sample of surface film. The second is surface film, mixed layer, and pycnocline. The third replicates the second, except that it includes samples from about 1,000 m, 2,000 m, 3,000 m, and near the bottom. The three spacings will be referred to as surface film, shallow array, and deep array and will involve one, three, and seven samples, respectively.

Surface film A set of 50 surface film samples should be collected, spaced generally over the ocean but with emphasis on the major zones of precipitation and evaporation and along the major shipping routes (especially for oil).

Shallow arrays Samples should be taken in the major eastern and western boundary currents (about 16 positions) and at the eastern and western edges of the three oceans at the equator. This totals 22 arrays with 3 samples each, or 66 samples.

Deep array Samples should be taken in the centers of the major gyres and in the major mediterranean seas (Arctic, Gulf of Mexico, Mediterranean, Okhotsk, Bering, and Sea of Japan). With a central equatorial array for each ocean, the total is 20 deep arrays of 7 samples each, or 140 samples.

ORGANISMS

The expense of marine sampling limits the number of organisms that can be collected for a worldwide program designed to provide

base-line measurement of the amounts of man-made pollutants in the marine biosphere. The following are considerations of significance for a selective sampling program:

Geographic distribution of primary biological productivity
Geographic distribution of world fisheries
Sites of major river outflows
General air-circulation patterns
Sites of major downwelling and upwelling of water
Sites of centripetal centers of major water gyres
Desired coverage of marine populations of organisms
Ease of sampling
Cost

The collection of adequate samples of marine organisms is important in areas of high primary productivity and major fisheries since several of these areas are near sites of dense human population and pollution production, support relatively large marine biomasses that may serve as reservoirs with slow turnover rates for pollutants, and provide food pathways leading to man through his utilization of marine fishery products.

The world catch of marine food is not evenly distributed throughout the seas and is composed of a great variety of marine species. In addition, many pollutants toxic to man are concentrated in unknown degrees in many marine species. These factors complicate the problem of collecting adequate and representative samples within the limitations of manpower and budget. Further complication is provided by the log-normal frequency distribution of amounts of trace pollutants and other trace materials that occurs in apparently homogeneous populations of organisms, including those from the marine biosphere (Ting and deVega, 1969). Because of these problems, edible parts of 10 to 20 individuals of each selected species collected at a given site (demersal and pelagic fish, mollusks, and crustacea) should be combined into a homogenized, pooled sample. Also, net plankton should be collected at selected sites.

The geographic distribution of primary productivity and world fisheries, shown in Figure A-1, are based on reports of Isaacs (1969) and Holt (1969). The major areas of high productivity include the Antarctic oceans, the North Atlantic banks, other shallows, and, of less importance, the outflows of rivers. The location of major fisheries depends upon the biological productivity and resulting food webs in

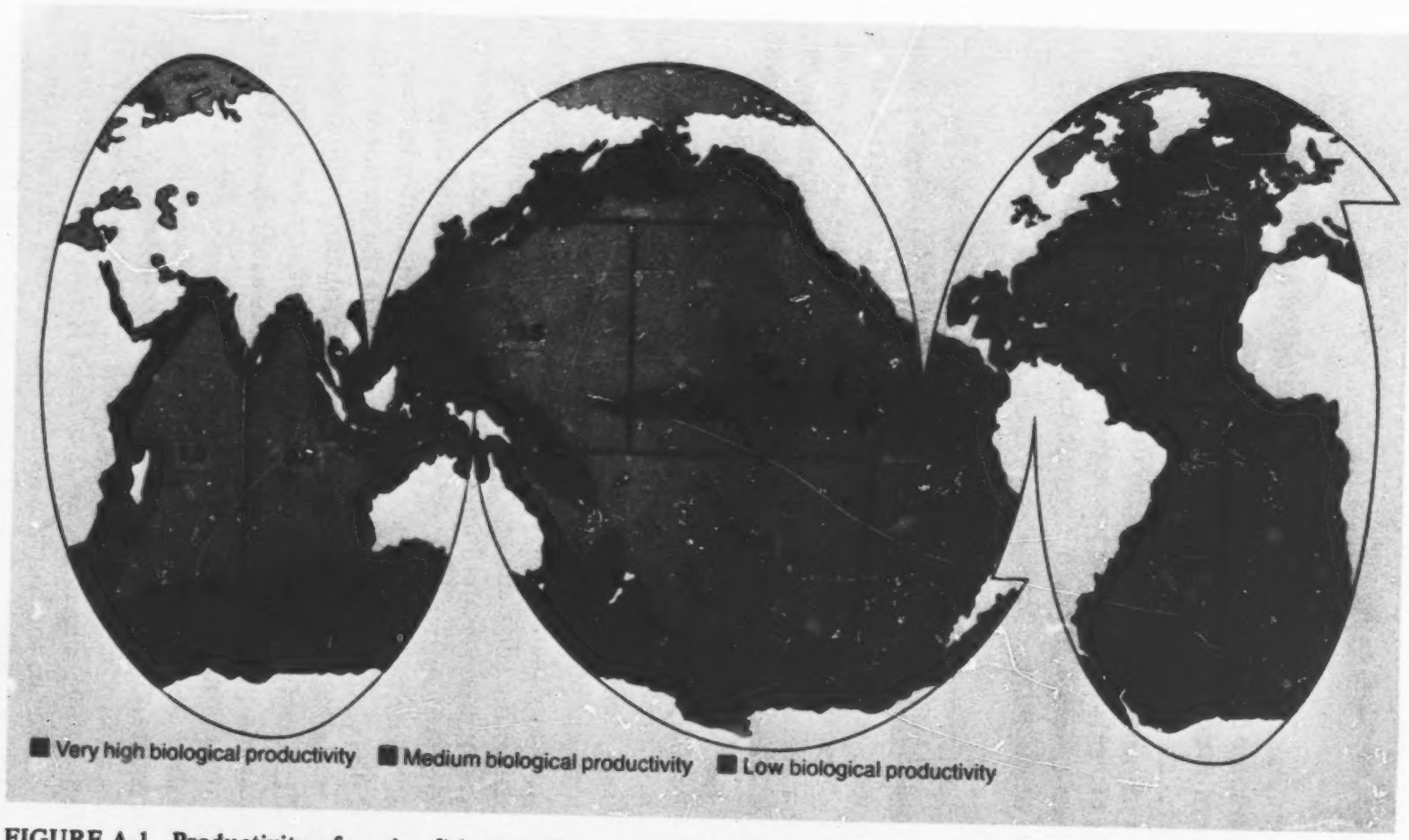

FIGURE A-1 Productivity of marine fisheries. The number that appears within each oceanic subdivision indicates the quantity (in metric tons) of fish landed in 1967.

the foraging areas. In addition, the catch is dependent upon the fishing effort. The landing of fish, in millions of metric tons, during the year 1967 were as follows:

Area	Millions of Tons	% of Total Catch	Area	Millions of Tons	% of Total Catch
NW Atlantic	4.0	7.6	N Pacific	6.4	12.2
NE Atlantic	10.2	19.5	W Central Pacific	10.5	20.0
W Central Atlantic	1.3	2.5	E Central Pacific	0.7	1.3
E Central Atlantic	1.6	3.1	SE Pacific	11.2	21.5
SW Atlantic	1.3	2.5	SW Pacific	0.4	0.8
SE Atlantic	2.5	4.8	W Indian Ocean	1.3	2.5
			E Indian Ocean	0.8	1.5

The fisheries of the northeast Atlantic, west central Pacific, and southeast Pacific accounted for 61 percent of the 1967 marine fishery and, with the north Pacific and northeast Atlantic, for more than 80 percent of the total. More than 65 percent of the Atlantic catch was taken above 30°N; the major sources of pollution in the Atlantic are also located north of this parallel.

Most of the major fisheries described above are found on or near the continental shelves. The stations of the sampling pattern shown in Figure A-2 are located mainly on the continental shelves at sites of high productivity, major fisheries, the outflows of major rivers, and at the sites of downwelling and upwelling of water. In addition, sampling stations are placed in the Mediterranean Sea and off the southern shores of Africa, Australia, and South America. This plan calls for the collection of 42 composite samples each of demersal fish, mollusks, and pelagic fish and 12 composite samples of benthic crustacea—a total of 138 samples.

Except for two sampling stations in the central Pacific, downcurrent from upwelling areas off the Pacific coast of South America, the central oceanic areas are not sampled because of their great average depth, which precludes sampling of demersal organisms, and the greatly reduced populations, and sporadic occurrence, of pelagic fishes. Although tunas and other fishes are sometimes taken in these areas, the lack of appropriate catch data from fishing boats operating in the central oceans and the limited knowledge of the migration habits of these fishes complicate the interpretation of data derived from these samples.

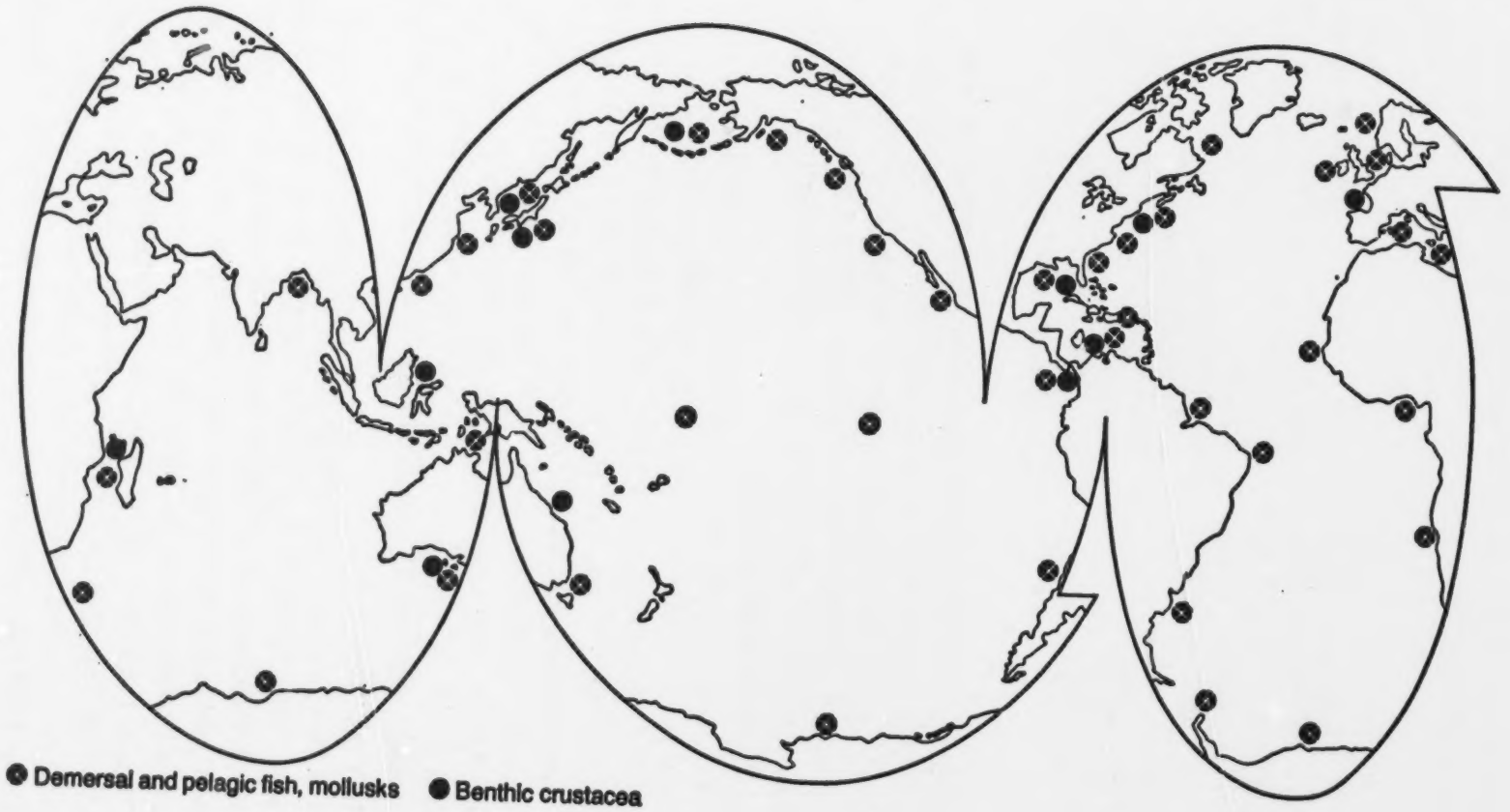

FIGURE A-2 Fish, mollusk, and crustacea sampling areas. Derived from Holt (1969) and Isaacs (1969). [Copyright © Massachusetts Institute of Technology 1970. Reprinted with permission from Study of Critical Environmental Problems (SCEP), 1970.]

Net plankton and flying fish, however, may be collected from the central oceanic regions (Figure A-3). Plankton may be taken on a predetermined grid, and sufficient flying fish normally come aboard research vessels operating in these regions at night to supply adequate samples for these areas. A total of 142 plankton samples and 40 flying fish (or more, if available) should be collected from the Atlantic, Pacific, and Indian oceans and the Mediterranean Sea.

In summary, the suggested program for marine organisms would consist of the following samples:

Fish	124
Mollusks	42
Crustacea	12
Plankton	142
Total	320

RIVERS

Various types of wastes are carried to coastal oceans by rivers. Identification of major routes and reservoirs requires that river water, river-borne sediment, and related sediment deposits be sampled during base-line studies. For the initial study, a limited number of areas are suggested. Criteria used for their selection are listed below:

Rivers
- Large river
- Extensive human activity
  - Industrial
  - Agricultural
- Different climatic zones
- Different stages of industrial development

Continental Shelf Areas
- Accumulation areas for modern sediments
- Areas used for other activities, such as fisheries
- Near rivers affected by man's activities, either industrial or agricultural

Samples of water and sediment should be composited in space and time. This procedure permits an estimate of concentrations for quasi-steady-state releases and should work well for dissolved (or dispersed) constituents. For rivers, two sampling periods are suggested—high-flow and low-flow stages—each of 6 months' duration.

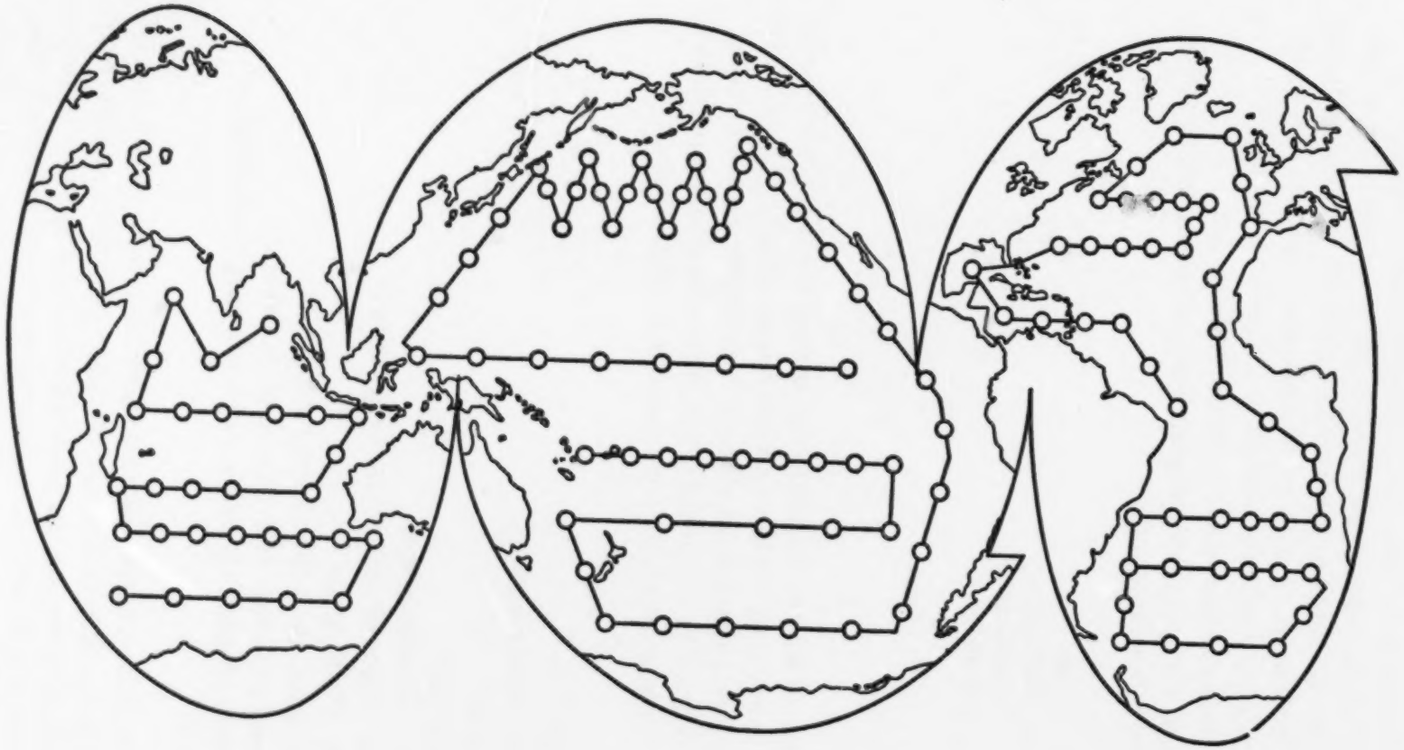

FIGURE A-3 Net plankton stations. [Copyright © Massachusetts Institute of Technology 1970. Reprinted with permission from Study of Critical Environmental Problems (SCEP), 1970.]

The amount of sediment transported by rivers is extremely variable. In most rivers, sediment moves primarily during a few weeks of maximum river flow. Hence, composite samples provide minimal data on annual sediment-transport phenomena.

River water and sediment samples should be collected in volumes proportional to river flow and composited over a 6-month period. One sampler near the river surface (perhaps on a float) would collect river water. Another near the bottom would collect water and sediment.

Four samples a year from 19 river systems should be collected, totaling 76 samples per year. The number of samples taken in rivers could profitably be doubled to provide more information about time variability in such systems. The 19 river systems to be included in the study are listed below.

North America
- Hudson
- Mississippi
- St. Lawrence
- Columbia

South America
- Orinoco
- Amazon
- Plata

Africa
- Nile
- Congo
- Niger

Europe
- Rhine
- Danube
- Po
- Thames

Asia
- Ganges–Brahmaputra
- Yellow (Hwang Ho)
- Amur
- Ob
- Indus

Floods are probably a major factor in flushing sediment out of estuaries. The proposed composite samples will not provide adequate samples of these important periods. Special samples should be collected from recently deposited sediments at the head of the estuary. For example, a sample might be taken from navigation channels farthest from the ocean. The sample should be typical of riverborne sediment and wastes accumulating in the estuary (the materials most likely to be removed by dredging or washed out by floods).

To understand the movement of sediment particles away from a river mouth, it is necessary to study deposits on the adjacent continental shelf or associated delta. Eleven areas, including four delta systems, are suggested for inclusion in the base-line study.

Yellow Sea
Mississippi Delta
Nile Delta
Baltic Sea
Sea of Japan
Ganges-Brahmaputra Delta
Tokyo Bay
Osaka Bay
North Sea
Black Sea
Rhone Delta

Several are associated with the major rivers included in this study. Others (such as the Sea of Japan or the two Japanese bays) were selected because of the importance of the regions as highly industrialized areas. The limited number of samples (approximately 50) should be composited to permit estimates of concentrations in recently deposited sediment.

GLACIAL, RAIN, AND SEDIMENT SAMPLES

An important record of the changed rates of waste injection into the atmosphere over the past several hundred years is contained in the permanent snowfields (glaciers). The glaciers occur over a wide range of latitudes, permitting an examination of fallout from all of the major wind systems. Time marks can be retrieved from the glacial record by lead-210 geochronologies, firn stratigraphy, or oxygen isotopic stratigraphy. The variations in oxygen isotopic compositions of glacial waters allow the yearly sequences to be subdivided into summer and winter periods. Such a subdivision may be useful in isolating the sources of introduced materials, as wind directions vary from one season of the year to another. At the present time, there are no well-documented techniques for making such historical studies on river influxes of materials. The following examples of glaciers that might be assayed, and the winds they monitor, have in most cases already been studied experimentally as recorders of atmospheric transport:

Glacier	Wind System
Greenland	Northern hemisphere polar easterlies
Yukon Territory or Mount Olympus, Washington	Northern hemisphere jets
Mt. Orizaba or Mount Popocateptl, Mexico	Northern hemisphere trades
Andean glaciers	Southern hemisphere trades
Tasman glaciers, New Zealand	Southern hemisphere jets
Antarctica	Southern hemisphere polar easterlies

A sampling program of these six zones is proposed to collect glacial ice samples representing 1970 summer and winter, 1969 summer and winter, 1968 summer and winter, 1965, 1960, 1953, 1943, 1930, 1900, and 1800.

For each of the trade and jet systems in the northern and southern hemisphere, composite rain samples (perhaps, a year's collection of rainwater) collected at single locations in both the Pacific and Atlantic oceans would be most useful for comparison with the glacial results and for measuring precipitation washout.

We propose that 78 permanent-snowfield samples and 48 rain samples be gathered.

Deep-sea sediments accumulate at extremely slow rates, fractions of a millimeter to centimeters per thousand years. These deposits are composed of rock debris from the continents, volcanic materials and their degradation products, oceanic precipitates such as the ferromanganese minerals and barite, and animal and plant frustules. Often, sediment surfaces are disturbed by burrowing organisms or near-bottom currents, phenomena that can introduce long time-period smears into the record. Thus, the utility of an extensive sampling program for deep ocean sediment is questionable.

On the other hand, fossil remains, including calcareous and siliceous tests, provide a measure of the removal of materials from surface waters to the sediments by biological agencies. A suite of four samples each of siliceous and calcareous ooze from the Pacific, Indian, and Atlantic oceans can provide a most reasonable set of base-line materials.

SUMMARY

The proposed base-line sampling program outlined above is, of necessity, intuitive. However, even before attempting to collect and analyze all the samples, it would be worthwhile to look at a much smaller number of samples as soon as possible, with the expectation that a more effective, and less expensive, base-line grid could be derived.

Although the program suggested is relatively simple and within reasonable financial and technological bounds, it can produce needed data on concentrations of potentially toxic pollutants in the marine environment. With this data, we can better judge the present and future impacts of chlorinated hydrocarbons upon marine ecosystems.

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Appendix B Identification of Globally Distributed Wastes in the Marine Environment

We propose a set of base-line measurements to identify distributions and concentrations of man-introduced materials in the atmosphere and ocean. Such a program can define present or potential threats to the continued survival and well-being of marine ecosystems. Already, mercury, halogenated hydrocarbons, and oil have been widely recognized. We seek to identify other materials of comparable significance.

Attention is focused primarily on atmospherically transported materials for several reasons:

River-carried solids are extremely diverse in type and are deposited primarily near the river mouth

Background concentrations of natural riverborne particles are large and variable and can therefore mask man's contributions

Airborne materials are widely dispersed over oceanic areas within days or weeks after injection into the atmosphere

To simplify the difficult problem of designating those materials that may pose problems to the marine environment, we have grouped them into three categories:

Particles from the combustion of fossil fuels and from industrial activities

Elements introduced to the atmosphere in amounts comparable to those brought to the world's rivers by natural processes

Synthetic organic chemicals

Table 1 makes it clear that a modern industrial society can now compete with natural processes as a source of materials in the environment. Although the available data are poor in quality, they suggest that burning fossil fuels will have a significant impact on the marine environment. Energy production is accompanied by emission of many other materials that may be detrimental to the environment; therefore, some measure of fossil-fuel combustion seems essential. Further, by tracing the paths of materials introduced to the atmosphere by energy generation, we can more readily ascertain the fates of other materials simultaneously introduced.

Elemental carbon (released as soot and cokey balls) formed by fossil-fuel combustion is disseminated by winds over the earth's surface. Rains over England contain elemental carbon that covaries with their sulfate contents in appreciable amounts (Gorham, 1955); both materials apparently came from the burning of coal. Atmospheric dusts collected over the Atlantic Ocean also contain elemental carbon, attributed to fossil-fuel burning (Folger, 1970).

TABLE B-1 Particles Injected into the Atmosphere by Natural and Artificial Processes

Process	Particles Injected into Atmosphere (g/yr)
Natural processes	
Continental rock debris	10^{14}–10^{15}[a]
Sea salt	10^{15}[b]
Volcanic emanations	10^{14}[c]
U.S. industrial, agricultural, and social releases[d]	
Total	10^{14}
Transportation	2×10^{12}
Fuel combustion	36×10^{12}
Industrial	15×10^{12}
Agricultural	54×10^{12}

[a] Goldberg, unpublished data.
[b] Study of Critical Environmental Problems (SCEP), 1970, p. 278.
[c] Windom *et al.*, 1967.
[d] National Air Pollution Control Administration (NAPCA), 1970.

Elemental carbon can be determined in atmospheric dusts and rains as part of the base-line program. Further, the historical record of fossil-fuel burning probably is held by the annual ice strata preserved in glaciers.

The simultaneous measurement of sulfate and carbon would give a broad picture of the fates of fossil-fuel emissions in the atmosphere. Sulfur initially introduced as sulfur dioxide and later oxidized to sulfate may have a somewhat different path in the atmosphere than that of carbon. To confirm the fossil-fuel origins of the elemental carbon and sulfate, isotopic analyses of sulfur and carbon could be used.

The contribution of gas and oil relative to that of coal may be found in assays for the aluminosilicate mullite made during the burning of coals. This mineral is detectable in fly ash (fine-grained ash) and is not normally found in rocks (Gross, 1971). Being rare in the environment, it may well be useful as a tracer of coal-combustion products.

Most of the particles generated by processes included in Table B-1 are large and therefore fall out close to their sources. Smaller particles with dimensions of microns or less may have long residence times in the atmosphere and may travel great distances before entering the ocean, where they can affect plant and animal populations.

Another group of chemicals encompasses those elements that are injected into the atmosphere at annual rates comparable to those in the major sedimentary cycle. In the latter case, compounds of the element are brought to the oceans by rivers. The chemical forms introduced by man may be different from those naturally present, and they may have an unusual size distribution or shape if they come in as solids. In any case, they can create new chemical surroundings for the marine organisms. The five metals included in Table B-2 fall within this classification.

The lead emission to the atmosphere results primarily from the combustion of lead tetraethyl and lead tetramethyl in gasoline; this accounts for about 20 percent of the total world usage of lead. Vanadium and nickel come from burning of fuel oil, where they are naturally bound in porphyrin complexes. Mercury is introduced to the atmosphere primarily through stack gases from caustic-chlorine plants where it is used as an electrode in the dissociation of saline solutions. Some mercury escapes during its use as a biocide in agricultural and industrial applications.

It is estimated that about half of man-induced emissions of cadmium to the atmosphere result from processing cadmium ores;

TABLE B-2 Mobilization of Elements at the Earth's Surface (g/yr). (Man-made emissions for mercury and lead are on a worldwide basis; for the other metals, U.S. values are given.)

Element	Natural Emission[a]	Industrial Emission	Approximate Value ($)[f]
Cd	3.1×10^8	2.0×10^9[b]	10,000,000
Hg	5.0×10^9	4.0×10^9[c]	50,000,000
Ni	2.0×10^{11}	7.0×10^9[b]	15,000,000
Pb	2.1×10^{11}	4.0×10^{11}[d]	20,000,000
V	2.8×10^{11}	5.0×10^9[e]	2,000,000

[a]Goldberg, 1965.
[b]National Air Pollution Control Administration, unpublished document.
[c]Klein and Goldberg, 1970.
[d]C. C. Patterson, personal communication.
[e]V. I. Blazingstoke, personal communication.
[f]U.S. Bureau of Mines, 1968.

cadmium is also lost in the mining and processing of zinc, lead, and copper ores. Another source of cadmium to the atmosphere is incineration of cadmium-containing waste products. This probably equals the loss resulting from the original processing.

The quantity of sulphur released to the atmosphere may be approximated from the following argument: Of the synthetic organic chemicals, 95 percent are produced from petroleum and require 5 percent of the annual world production of petroleum (50 million tons per year in the United States). In addition, there is a substantial loss of hydrocarbons through fuel combustion, transportation, industrial processes, and solid waste disposal (Table B-3).

Several criteria are suggested for use in selecting synthetic organic substances for inclusion in a base-line program:

The material is produced and may enter the atmosphere or ocean in large quantities.

The material (or its degradation products) interferes with metabolic activities of one or more forms of life.

The material is concentrated by one form of life on which it may have no discernible effect, but which is food for another form of life on which it can have a most deleterious effect. The passage of DDT and its residues through the food chain and their subsequent effect upon bird and fish populations illustrates such a case.

Its physical form interferes with an organism's growth, activity, or

TABLE B-3 Organic Chemicals–Some Production and Potential Emission Data for United States[a]

Substance	Present Production Rate (g/yr)	Emission Rate (g/yr)
Total amounts of synthetic organics	5×10^{13}	–
DDT	2×10^{11}	–
PCB's	5×10^{9}	–
Dry-cleaning solvents, perchloroethylene and trichloretheylene	2×10^{11}	2×10^{11}
Freon-12 (CCl_2F_2)	1×10^{11}	1×10^{11}
Gasoline into atmosphere		2×10^{12}
Hydrocarbons lost in transportation, fuel combustion, industrial processes, solid waste disposal, etc.	–	3×10^{13}
Petroleum introduced directly into marine environment by man's activities	–	3×10^{12}

[a]Goldberg, unpublished data.

well-being. For example, asbestos fibers and siliceous particles cause damage to man's lungs.

The material or its decomposition products is alien to the marine environment but similar to substances that have known teratogenic, mutagenic, toxic, or carcinogenic effects. For example, the dry-cleaning solvent, trichloroethylene, may affect enzyme activities as do the heavier chlorinated hydrocarbons.

A sense of priority for the inclusion of synthetic organic chemicals in a base-line program may be established by using such criteria in combination with the chemical and biochemical characteristics of a given substance. This suggests that special attention be given halogenated organic compounds.

The 2.1 million tons per year of petroleum introduced directly into the marine environment [Study of Critical Environmental Problems (SCEP), 1970, p. 267] provides a special case of a substance to be measured. Much of this material, introduced into coastal waters, estuaries, harbors, and shipping lanes, may accumulate in the air–water interface to form slicks. Such a veneer over the ocean may be

a site of uptake of nonpolar organic materials transported about the atmosphere or the surface ocean.

Hydrocarbons appear to constitute a major emission of organic compounds to the environment and can be globally dispersed by wind systems. Since northern hemisphere emissions vastly exceed those from the southern hemisphere and since most industrial activity is at midlatitudes, it is necessary to focus attention upon midlatitudinal oceanic areas in the northern hemisphere. With halogenated hydrocarbons, entry through the atmosphere to the ocean probably involves a reservoir at the air–water interface. Natural substances forming such surface films include fatty acids and their alcohols; man-introduced materials consist of oil from leakages and spills. Such a surface film may pick up many of the other organic compounds translocated from the continents to the oceans via the atmosphere.

Thus, in preparing a set of base-line measurements to identify distributions and concentrations of man-introduced materials in the atmosphere and ocean, attention should be directed to the analysis of a variety of organic compounds in surface films, such as DDT and its residues, freon, and gasoline hydrocarbons.

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Persistent chlorinated hydrocarbons, Marine environment, Half-life

27 **Abstract**
The oceans are the ultimate accumulation site for the persistent chlorinated hydrocarbons. As much as 25 percent of the DDT compounds produced to date may have been transferred to the sea. The amount of DDT compounds in the marine biota is estimated to be less than 0.1 percent of total production, yet this amount has produced a noticeable impact upon the marine environment. The rate at which such substances degrade to harmless products in the marine system is unknown; the half-lives of some of the more persistent materials are of the order of years, and perhaps even decades and centuries. If most of the remaining 75 percent of the persistent chlorinated hydrocarbons is in reservoirs that will in time transfer their contents to the sea, we may expect an increased level of these substances in marine organisms. It is recommended that: (1) A massive effort should be made immediately to check the escape of persistent toxicants into the environment, (2) rates of entry of each pollutant into the marine environment be determined and (3) the laws relating to the registration of chemical substances and the release of production figures by the government be examined.
(Ensign - PAI)

The report discusses the fact that ... The report presents material to support its recommendations

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